Chem 4A, Fall 2006
Midterm exam 3, November 17, 2006
Prof. Head-Gordon; Prof. Moretto

Name: **COMPUT KEY**  TA: _____________________________

Grade:  
1. (7 points)  
2. (1 point)  
3. (4 points)  
4. (4 points)  
5. (3 points)  
6. (3 points)  
7. (3 points)  
Total:  

Close book exam. There are 6 pages. Calculators are OK. Use back side of pages for scribble paper.

Some possibly useful facts and figures:

\[ R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{molar volume at STP}= 22.4 \text{ L} \]

\[ k_B = 1.38066 \times 10^{-23} \text{ JK}^{-1} \quad N_0 = 6.0221 \times 10^{23} \text{ mol}^{-1} \]

For 1 mole of ideal gas:
\[ E = \frac{3}{2} RT \quad \text{C}_v = \frac{3}{2} R \quad S = \frac{3}{2} R \ln T + R \ln V \]

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \Delta H_f^0 ) (kJmol(^{-1}))</th>
<th>( S^0 ) (Jmol(^{-1})K(^{-1}))</th>
<th>( \Delta G_f^0 ) (kJmol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)(g)</td>
<td>-75</td>
<td>187</td>
<td>-51</td>
</tr>
<tr>
<td>O(_2)(g)</td>
<td>0</td>
<td>205</td>
<td>0</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>-286</td>
<td>70</td>
<td>-237</td>
</tr>
<tr>
<td>H(_2)O(g)</td>
<td>-242</td>
<td>189</td>
<td>-228</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>-395</td>
<td>214</td>
<td>-229</td>
</tr>
<tr>
<td>CaCO(_3)((s))</td>
<td>-1207</td>
<td>93</td>
<td>-1129</td>
</tr>
<tr>
<td>CaO((s))</td>
<td>-635</td>
<td>40</td>
<td>-604</td>
</tr>
</tbody>
</table>
1. (7 points) Given the unbalanced reaction:

\[ \text{CH}_4 + \text{O}_2 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}(l) \]

(a) (1 point) balance the equation

\[
\begin{align*}
\text{CH}_4 (g) + 2\text{O}_2 (g) & \leftrightarrow \text{CO}_2 (g) + 2\text{H}_2\text{O}(l)
\end{align*}
\]

(b) Start with 1.0 moles of CH\(_4\) and enough O\(_2\) to burn it completely. Calculate:

- (2 points) \( \Delta H^\circ \); \( \Delta G^\circ \)

\[
\Delta H^\circ = [\left( -395 \text{ kJ/mol} \right) + 2(-286)] - [\left( -75 + 2(0) \right)] = -892 \text{ kJ/mol}
\]

\[
\Delta G^\circ = [\left( -229 \text{ kJ/mol} \right) + 2(237)] - [\left( -51 + 2(0) \right)] = -652 \text{ kJ}
\]

- (2 points) the initial and final volume at 1 Atmosphere and 25\(^\circ\)C

(volume of 1 mol ideal gas at STP (1 atm, 0\(^\circ\)C) = 22.4 L (Sircar, p. 29))

\[
\text{volume, initial: (3 mol)} \times \left( \frac{22.4 \text{ L}}{273 \text{ K}} \right) = 73.4 \text{ L}
\]

volume, final 1 mol \( \rightarrow \frac{1}{3} V_i = \frac{24.5 \text{ L}}{3} \)

- (2 points) the final temperature if you keep the initial volume fixed and the container isolated (Assume only translational degrees of freedom). Should you take into account water molecules?

\( \Delta H^\circ \) for H\(_2\)O (g): \[ \left( -395 \text{ kJ/mol} \right) + 2(-242) \neq -75 + 2(0) \] = -804 kJ

\[
E = \frac{3}{2} kRT = \frac{3}{2} (3 \text{ mol gas now!!}) (273 \text{ K}) = \frac{9}{2} R = 37.4 \frac{1}{\text{ mole} \cdot \text{ K}}
\]

\[
E = -\Delta H^\circ = +804 \text{ kJ} = \frac{3}{2} kR \Delta T = \frac{9}{2} R \Delta T = 37.4 \frac{1}{\text{ mole} \cdot \text{ K}} (\Delta T)
\]

\[
\Delta T = 21.489 \text{ K} \quad \text{(final temperature)} = 298 \text{ K} + \Delta T = 21,787 \text{ K}
\]
2) (1 point) A heat pump is used to keep a house at 25°C. The outside temperature is 0°C. Calculate the efficiency of an ideal heat pump. (Hint: it has better be >1!)

\[ \varepsilon = \text{heat out} / \text{(electrical energy in)} \]

\[ \text{Efficiency of heat pump} = \frac{T_1}{T_1 - T_2} = \frac{298}{298 - 273} = \frac{11.92}{11.27} \]

- \( T_1 = \text{larger temp} = 298 \text{ K} \)
- \( T_2 = \text{smaller temp} = 273 \text{ K} \)

3) (4 points) One mole of ideal gas at temperature \( T \) and volume \( V \) is expanded isothermally and reversibly to volume \( 2V \).

- (2 points) Calculate \( \Delta S \)

\[ \Delta S = nR \ln \frac{V_2}{V_1} = (1 \text{ mol}) (R) \ln \left( \frac{2V}{V} \right) \]

\[ \Delta S = nR \ln 2 = R \ln 2 = 5.76 \text{ J/mol K} \]

- (2 points) The same initial gas is adiabatically expanded with no external work to the same volume \( 2V \).
Calculate \( \Delta T \) and \( \Delta S \).

"adiabatic" : \( q = 0 \)

\[ \Delta E = q + w = 0 + 0 = 0 \]

\[ \Delta E = \frac{3}{2} nR \Delta T \rightarrow \Delta T = 0 \]

\[ \Delta S = R \ln 2 = 5.76 \text{ J/mol K} \text{ is state function} \]

\( \rightarrow \text{Same as above value for} \Delta S \)
4) (4 points) You toss 10 quarters of which \( n \) turn out heads. Each head will cost you the quarter. (cost is like energy)

- (2 points) Write down the entropy \( S \) as a function of the total cost (energy).
  No calculations are needed

\[
S = k \ln \Omega, \quad \Omega = \frac{N!}{n! (N-n)!}
\]

\[
N = 10 \quad \Rightarrow \quad S = k \ln \frac{N!}{n! (N-n)!} = k \ln \frac{10!}{n! (10-n)!}
\]

\[
E = 0.25 \cdot n \quad \Rightarrow \quad n = \frac{E}{0.25}
\]

\[
S = k \ln \frac{10!}{(E/0.25)! (10-E/0.25)!}
\]

- (2 points) Can you figure out for which \( n \) is \( S \) maximum? (you can get the answer just by inspecting the formula)

\[
S = k \ln \frac{N!}{n! (N-n)!}
\]

Note: This value must be greater than or equal to \( 1 \) by the value. Also, \( \ln(0) \to -\infty \), so this value must be \( >1 \); and note that \( \ln(1) = 0 \)

\[
\begin{align*}
\text{if} \quad n = 0, \quad \Rightarrow & \quad \frac{10!}{0! (10-0)!} = \frac{10!}{10!} = 1 \\
\text{if} \quad n = 10, \quad \Rightarrow & \quad \frac{10!}{10! (10-10)!} = \frac{10!}{10!} = 1 \\
\end{align*}
\]

\( \therefore \) minima occur @ \( n = 0, 10 \); if \( S \) is symmetric, then

maximum occurs @ \( n = 5 \)
5) (4 points) Consider the reaction

\[ \text{CaCO}_3(s) \leftrightarrow \text{CaO}(s) + \text{CO}_2(g) \]

- (2 points) Calculate \( \Delta H^0 \), \( \Delta S^0 \) and \( \Delta G^0 \). Is the reaction spontaneous at standard conditions?

\[
\Delta H^0 = (-635 \text{ kJ/mol} + 395 J) - (-1207 J) = 177 \text{ kJ}
\]

\[
\Delta S^0 = (40 \frac{\text{J}}{\text{mol} \cdot \text{K}} + 214 J) - 93 J = 161 \text{ J/K}
\]

\[
\Delta G^0 = (-604 \frac{\text{kJ}}{\text{mol}} + 229 J) - (-1127 J) = 226 \text{ kJ}
\]

Reaction is not spontaneous @ STP \( \because \Delta G^0 > 0 \)

- (2 points) Assuming \( \Delta H^0 \) and \( \Delta S^0 \) to be temperature independent, estimate at what temperature \( \Delta G = 0 \)

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

\[
0 = 177 \text{ kJ} - T (161 \text{ kJ/K})
\]

\[
T = 1099 \text{ K} = 826 ^\circ \text{C}
\]
6) (3 points) The solubility product of AgCl is $K_{sp}=10^{-10}$. Calculate:

- (1 point) the solubility of AgCl in pure water

$$\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1 \times 10^{-10}$$

$$= [S^2] [S] = 1 \times 10^{-10} = S^2$$

$$S = \sqrt{K_{sp}} = \sqrt{1 \times 10^{-10}} = 1 \times 10^{-5} \text{ M}$$

- (2 points) the solubility of AgCl in a 1.0 M NaCl.

$$\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \quad (1.0 \text{ M NaCl} \rightarrow 1 \text{ M Na}^+ + 1 \text{ M Cl}^-)$$

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1 \times 10^{-10}$$

$$= [S^2] [1.0 \text{ M}] = 1 \times 10^{-10}$$

$$\therefore S = 1 \times 10^{-5} \text{ M}$$

7) (3 points) Sulphur has four phases: rhombic, monoclinic, liquid, gas. By means of Gibbs' rule calculate the maximum number of phases that can coexist. In a P,T phase diagram identify the triple points, the coexistence lines, and the variance in the relevant parts of the diagram.

**Gibbs' Phase Rule:**

$$V = n - f + 2$$

$$\theta = f - 3 = \text{max \# phases that coexist}$$

**Triple Point(s):**

- $T_1$: rh, mo, vapour
- $T_2$: mm, liquid, vapour
- $T_3$: rh, mo, liquid